

5 **SPECIFICATION**

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10 **TITLE: CURABLE EXTRUDED ADHESIVE LAMINATE SYSTEM FOR
MANUFACTURING COLLAPSIBLE STRUCTURES**

BACKGROUND

15 **FIELD OF THE INVENTION**

The invention relates generally to flexible laminates and more particularly to extruded thermoplastic adhesive laminates, wherein the laminate is particularly suitable for 20 forming collapsible structures such as fuel tanks, water tanks, inflatable boats and other solid/liquid storage tanks.

PRIOR ART

Traditionally, collapsible tanks are constructed of panels that are assembled into the 25 desired shape either by compression press or hot-air heating and pressure or RF welding. Flexible laminates are made by applying a solvent based adhesive on a nylon or polyester or Kevlar fabric, which is then extrusion coated with a thermoplastic polyurethane (TPU) or a TPU alloy onto the adhesive side of the coated fabric. In the current art the solvent based adhesive typically has a curing additive which cross-links the adhesive, thereby securely 30 anchoring the extruded TPU to the fabric. It is recognized that the collapsible structures can undergo rather severe oxidative and hydrolytic conditions. As an example, in a water tank, the water tank can be exposed to the external weather elements for an indefinite, and potentially extended, period of time. Also, the collapsible structures used as fuel tanks need

to be resistant to the solvating effects of fuel and, therefore, must be virtually impervious and non-swelling in the presence of the fuel. In both cases a relatively high-degree of cross-linking is desired to minimize the deleterious effects of fuel, oxygen, and water. To a certain extent the TPU is selected so that it is inherently resistant to aging, hydrolysis, 5 oxidation and swelling. Typically, the adhesive laminate, as well as the assembled tank or other collapsible structure needs to retain bond strength and seam strength under severe conditions. The minimum acceptable bond performance is 25 lbs/in, following immersion in water and/or fuel at 160°F for six weeks.

10 While conventional solvent based adhesives meet the performance requirements for collapsible structures there are various process-related problems. The major concern is the generation of air-borne emissions, typically as defined by the EPA as VOCs (e.g. volatile organic compounds). Normally, VOCs are captured by solvent recovery systems, or are disintegrated using catalytic converters (a.k.a. thermal oxidizer). Solvents have the 15 additional problem that in addition to their cost of use and cost of capture they are flammable, and therefore represent an on-going threat of fire. What is desired is a laminating adhesive suitable for collapsible structures that does not utilize a solvent-based adhesive.

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SUMMARY OF THE INVENTION

The invention is a heat-curable extruded adhesive laminate system for producing collapsible tanks. The system is comprised of a fabric, onto which is coated an extruded

adhesive having a latent thermally activated curing component; and then onto which is coated a thermoplastic resin. The thermoplastic resin is extruded on top of the extruded adhesive. Alternatively, the thermoplastic resin and adhesive can be co-extruded onto the fabric. The adhesive can also be applied with a slot die or hot melt coating equipment. The 5 thermally activated curing component remains latent until the laminate system is elevated to a temperature that is sufficiently high to actuate the curing component. Examples of latent thermally activated curing components are blocked isocyanates, which are isocyanates that are reversibly reacted with ketoximes, hydroxylic compounds such as 1,2,4-triazole, 3,5-dimethylpyrazole, and cycloimides, such as epsilon-caprolactam. Another type of blocked 10 isocyanate are those characterized as internally blocked isocyanates. They are substantially dimers of diisocyanates. The dimers, as a class, are known as uretdiones. Some commercial grades include multi-uretdione adducts, as well as pure dimers, or a combination thereof. Uretdione diisocyanates are selected from the group consisting of TDI, MDI, XDI, IPDI, H₁₂MDI and HMDI. The aliphatic and cycloaliphatic diisocyanates are particularly suited 15 for the invention in that they have superior weathering. An example of an aliphatic diisocyanate is hexamethylene diisocyanate (HMDI), and prototypical of cycloaliphatic diisocyanates are isophorone diisocyanate (IPDI) and hydrogenated HMDI, also known as dicyclohexalmethene 4,4'-diisocyanate (H₁₂MDI). Uretdiones, upon heating, disassociate to form the monomers at temperatures normally used to assemble panels of the heat-curable 20 extrudable adhesive laminate. Seaming bonds of panels are typically formed in a compression press at temperatures from about 260°F to about 350°F, wherein the combination of heat and pressure cause the thermoplastic resins and adhesive to fuse and cure. Typical press times are on the order of 20 to 45 minutes. It is recognized that higher temperatures can be employed; however, potentially with disadvantageous side reactions.

Preferably, the thermally activated curing component additionally comprises a cross-linking enhancer which is commonly a multi-functional hydroxyl compound. Examples of cross-linking enhancers are hydroxyalkyamides (i.e. N,N,N',N'-tetrakis(2-hydroxyethyl)adipamide, or N,N,N',N'-tetrakis(2-hydroxypropyl) adipamide); triglycidyl isocyanurate, pentaerythritols; mono, di and tri alkanol amines; glycols; abitol; butylene glycol; cyclohexandeminethanol; dipentaerythritol; dipropylene glycol; glycerine; hexylene glycol; hydrogenated Bisphenol A; methyl 1,2 propanediol; neopentylglycol; propylene glycol; sorbitol; triethylene glycol; trimethylolpropane; tripentaerythritol; alkoxy and hydroxyl alkoxy cellulose, simple sugars like fructose, sucrose, glucose and starches. Note, 5 in the case of some multi-functional hydroxy compounds there is an amine group that is a component of the compound. Amines are catalysts that accelerate the isocyanate reaction with a hydroxy functional group therein forming a urethane. It is anticipated that the heat curable extruded adhesive laminate system can be compounded to include urethane catalysts and accelerants, such as sterically hindered amines (i.e. DABCO® registered trademark of 10 15 Air Products) and metal catalysts. Examples of two commonly employed tin catalysts are stannous octoate and dibutyl tin dilaurate. Goldschmidt Industrial Chemical Corporation offers a more complete list of metal catalyst. The preferred thermoplastic resin is a thermoplastic polyurethane (TPU) or a TPU alloy that has a low to medium level of crystallinity. Likewise, the extruded adhesive is a thermoplastic polyurethane with a 20 medium to high degree of crystallinity. The extrudable adhesive is a hydroxyl thermoplastic urethane with pendent hydroxyl groups with which the latent thermally activated curing component can react, thereby cross-linking (in effect polymerizing) the adhesive. Following curing, the cross-linked adhesive is resistant to heat and to solvents. The heat curable extruded adhesive laminate can then be cut into panels for fabrication into collapsible tanks

and the like. The heat curable extruded adhesive laminate system further comprises the fabrication of the panels into collapsible tanks, such as water tanks and fuel tanks and puncture resistant fabrics having good weathering properties. These fabrics are sometimes referred to as ballistic fabrics, depending on their level of puncture resistance. An example 5 of an application for ballistic fabrics is in the fabrication of inflatable boats.

Alternatively, the extruded adhesive with the thermally activated curing component can be admixed with the thermoplastic resin, and the entire composition can be extruded as a one pass coating onto the fabric. We have found that the effectiveness of the admixture is 10 reduced; however, for certain less critical applications, where cost is a major consideration, a one pass process can be employed with varying levels of success. As the case with the two pass process and the co-extruded process, in a one pass heat curable extruded adhesive laminate system, the curing component is latent during extrusion, and is initiated when the laminate is exposed to the higher temperatures and longer elevated temperature times used 15 during the fabrication of the collapsible structures.

Irregardless of whether a one pass, a two pass or a co-extruded process system is employed, the thermoplastic resin and/or the extruded adhesive can be compounded with additional additives, such as reinforcing fibers, extenders which are fillers, antioxidants, UV 20 stabilizers, thermo-stabilizers, flame retardants, glass beads, colorants, anti-microbial agents, dyes, pigments, processing aids (i.e. waxes, fluorinated compounds, silicone compounds, surfactants, polymeric processing aides), density modifiers such as phenolic beads, desiccants, buffers, and IR absorbent compounds to facilitate heating. Examples of IR absorbent compounds are carbon blacks, graphite, and metal oxides, which can be added in

such levels as to be virtually non-coloring, yet absorbent to infrared radiation, which enables the laminate to be rapidly deep heated.

Depending on the structural requirements for the collapsible tank, the fabric is
5 selected to be sufficiently strong to handle the tensile requirements imposed by the weight of the contents of the tank. The invention is not limited to merely free standing tanks and inflated tanks. The collapsible tank can be supported by a frame or a palletized container.

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DETAILED DESCRIPTION

The invention is a heat curable extruded adhesive laminate system for producing
15 collapsible tanks. Examples of collapsible structures include fuel tanks, water tanks, inflatable boats and other solid/liquid storage tanks. Polyurethanes are preferred because of their flexibility, their inertness, and in the case of water tanks they can be synthesized so that there are very few residual materials that impart taste, and they can be selected to have good hydrolytic stability. In the invention, the laminate is a composite of a fabric, a heat curable extruded adhesive, and a thermoplastic polyurethane (or TPU) or TPU alloys. Typically, the fabric is selected from Nylon or polyester, albeit other materials are suitable. In the case of inflatable boats, ballistic cloth is normally used, and ballistic cloth usually incorporates polyimides (e.g. Kevlar® by Dupont) or Nylon or ultra high molecular weight polyethylene (UHMW polyethylene). The fabric can also be a blend of organic and/or inorganic fibers
20 (i.e. fiber glass). Nominally, the tanks are constructed by assembling panels of the extruded adhesive laminate into the desired shape. Compression press or hot-air or RF welding are the preferred techniques for seaming. The latent cure in the extruded adhesive is activated
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causing the extruded adhesive to be cured during the assembly operation. The preferred adhesive is a thermoplastic polyurethane containing reactive hydroxyl functional groups. The thermoplastic polyurethane has medium to high crystallinity. Examples of suitable elastomeric polyurethane adhesives are Bayer's Desmolmelt 540 and Desmolmelt 530.

5 Desmolmelt 540 is a linear hydroxyl polyurethane, where the polyurethane is of the polyester type. The hydroxyl content is less than 1%. The activation temperature is approximately 60°C. It is described as having a very high crystallinity and very low thermoplasticity. Desmolmelt 530 has a slightly lower activation temperature, approximately 55°C, slightly lower crystallinity and slightly lower molecular weight. The

10 adhesive is compounded with a latent isocyanate based cross-linker, a hydrolytic stabilizer and a cross-link enhancer. The isocyanate is internally blocked, preferably the uretdione type, which activates at temperatures in excess of 300°F. Uretdiones of IPDI are particularly suitable, as they are cycloaliphatic, and therefore are relatively non-yellowing. Commercial grades of uretdiones, which are poly-uretdiones of IPDI are CRELAN VP LS

15 2347, VESTAGON EP-BF-1320, VESTAGON BF 1540. VESTAGON® BF 1540 is a Degussa product. It is uretdione-poly adduct having an NCO content of 15.2–17.0% wt. VESTAGON EP-BF-1320 is also a uretdione-poly adduct, having an NCO content 13.0–14.5% wt. VESTAGON EP-BF-1320 has a higher functionality than BF 1540. It is supplied as a coarsely ground powder. CRELAN® VP LS 2347 and CRELAN® VP LS

20 2147 are Bayer uretdione "hardeners". The adhesive is further compounded with a cross-link enhancer, such as hydroxyalkylamide. Examples of a hydroxyalkylamide include N,N,N',N'-tetrakis(2-hydroxyethyl)adipamide, which is commercially sold under the brand name Primid XL-552, and N,N,N',N'-tetrakis(2-hydroxypropyl)adipamide, which is commercially sold under the name of Primid QM-1260. Primid® is a trade name of Ems-

Chemie AG, Switzerland. The disclosed hydroxyalkylamide has a functionality of four, and is very effective at increasing the cross-link density. The adhesive is further comprised of a hydrolytic stabilizer such as a carbodiimide. A suitable carbodiimide is bis(2,6-di-2-propylphenyl)carbodiimide, sold under the trade name of Stabaxol® of Bayer. Rhein

- 5 Chemie sells various grades of bis(2,6-di-2-propylphenyl)carbodiimide as masterbatches, which facilitates mixing. The preferred thermoplastic polyurethane is a high molecular weight polyester type thermoplastic TPU. Representative commercial grades that are suitable are ESTANE 58277, ESTANE 58226, ELASTOLLAN 695A15, PELLETHANE 2355, and DESMOPAN 285. ESTANE® is a registered trademark of Noveon, Inc.,
- 10 ELASTOLLAN® is a registered trademark of BASF Corporation, DESMOPAN is a registered trademark of BAYER Corporation and PELLETHANE® is a trademark of Dow. The preferred TPUs are polyester type polyurethanes having good hydrolytic stability, a Vicat softening point greater than 170°F, and a Shore A Durometer of greater than 88. The tensile is preferably greater than 5000 psi.

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In preparing the adhesive, a twin screw extruder can be used to compound all the components and then form pellets. The pellets are then extruded as a thin film onto the appropriate fabric, and then the TPU is extruded on the adhesive film. An alternative method is to co-extrude the adhesive and TPU together onto the fabric. The extrusion

- 20 temperature is adjusted so that minimum curing takes place inside the extruder. Extrusion laminates made in this fashion can be assembled using a compression press. The presses normally operate between 280-340°F and 20-45 minutes dwell times. The elevated temperatures cause the TPU on the panel of the laminate to weld to the TPU on adjacent

panels. During the assembly process, the uretdione activates and propagates the cross-linking reaction resulting in a long lasting, strong bond.

In the examples below are two examples of the adhesive formulation.

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Example 1

In a twin screw extruder are added 2000 wt. units of Desmomelt 540 (a linear hydroxyl polyurethane adhesive), 200 wt. units of Vestagon BF 1320 (uretdione internally 10 blocked cross-linked) and 12 wt. units of Staboloxol P (carbodiimide – hydrolytic stabilizer). The components are mixed and pelletized.

Example 2

15 In a twin screw extruder are added 1500 wt. units of Desmomelt 540 (a linear hydroxyl polyurethane adhesive), 150 wt. units of Vestagon BF 1320 (uretdione internally blocked cross-linked isocyanate), 12 wt. units of Staboloxol P (carbodiimide – hydrolytic stabilizer), and 50 wt. units of Primid (N,N,N',N'-tetrakis(2-hydroxyethyl)adipamide, a cross-link enhancer). The components are mixed and pelletized.

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Prior to extruding the thermoplastic resin (TPU), the TPU is dried. The water content is preferably less than 0.03%. Masterbatches of fillers, colorants, and reinforcing additives are compounded as desired. Nominally, additional antioxidants, UV stabilizers

and processing aides are not required. Coating weights are appropriately adjusted for the denier and count of the thread.

Following compression heating in the press, the resulting seams have a strength that

5 exceed the minimum acceptable bond performance of 25 lbs/in, following immersion in water and/or fuel at 160°F for six weeks.

It is to be understood that the foregoing description and specific embodiments are merely illustrative of the best mode of the invention and the principles thereof, and that

10 various modifications and additions may be made to the apparatus by those skilled in the art, without departing from the spirit and scope of this invention, which is therefore understood to be limited only by the scope of the appended claims.